



Single Electrode Heat Effects II. Single Electrode Heat Evolution

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Published in:
Journal of The Electrochemical Society

Link to article, DOI:
[10.1149/1.2133268](https://doi.org/10.1149/1.2133268)

Publication date:
1977

Document Version
Publisher's PDF, also known as Version of record

[Link back to DTU Orbit](#)

Citation (APA):
Jacobsen, T., & Broers, G. H. J. (1977). Single Electrode Heat Effects: II. Single Electrode Heat Evolution. *Journal of The Electrochemical Society*, 124(2), 210-214. <https://doi.org/10.1149/1.2133268>

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$$\Delta S_{P,rev^0}(\text{O}_2, \text{CO}_2) = S^0(\text{CO}_3^{2-}) - \frac{1}{2} S^0(\text{O}_2) - S^0(\text{CO}_2) - 2S^0(\text{e}^-) \simeq 191 \text{ J/mole}^\circ\text{K}$$

which is rather close to the experimental Peltier entropy of $-217 \text{ J/mole}^\circ\text{K}$. The uncertainties introduced by the assumptions made above may readily account for the discrepancy. Thus, as expected the entropies of transfer only constitute a minor part of the Peltier entropies of gas electrodes in molten carbonates.

Acknowledgments

The authors are indebted to F. Haslev and L. Christiansen for their participation in the experimental work. The many valuable discussions with B. K. Andersen and other colleagues are greatly appreciated. This work has been supported by Statens Teknisk Videnskabelige Fond.

Manuscript submitted May 27, 1976; revised manuscript received Aug. 1, 1976. This was Paper 171 presented at the New York, New York, Meeting of the Society, May 4-9, 1969.

Any discussion of this paper will appear in a Discussion Section to be published in the December 1977 JOURNAL. All discussions for the December 1977 Discussion Section should be submitted by Aug. 1, 1977.

LIST OF SYMBOLS

E	electromotive force (V)
F	Faraday constant (C/mole)
ΔH	enthalpy of reaction (J/mole)
p	partial pressure (atm)
t	transport number
T	temperature ($^\circ\text{K}$)
TEF	thermoelectric force (V)

TGF	thermogalvanic force (V)
S	entropy (J/mole $^\circ\text{K}$)
ΔS_P	Peltier entropy (J/mole $^\circ\text{K}$)
S^*	entropy of transported species (J/mole $^\circ\text{K}$)
$\Delta \bar{S}$	excess entropy of transported species (J/mole $^\circ\text{K}$)
ϵ	Seebeck coefficient (V/ $^\circ\text{K}$)
K	equilibrium constant

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Single Electrode Heat Effects

II. Single Electrode Heat Evolution

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ABSTRACT

The heat evolution at a single irreversibly working electrode is treated on the basis of the Brønsted heat principle. The resulting equation

$$\frac{dQ}{dt} = \left(T \frac{\Delta S_P}{nF} + \eta \right) i$$

is analogous to the expression for the total heat evolution in a galvanic cell with the exception that $-\Delta S$ is substituted by the Peltier entropy, ΔS_P , of the electrode reaction. η is the overvoltage at the electrode. This equation is applied to a high temperature carbonate fuel cell. It is shown that the Peltier entropy term by far exceeds the heat production due to the irreversible losses, and that the main part of heat evolved at the cathode is reabsorbed at the anode. Finally, effects like thermal corrosion, caused by internal temperature gradients, are discussed.

Most treatments of heat effects in galvanic cells are based on the over-all heat evolution calculated from the reversible heat evolution, $-T\Delta S$, and the polarization losses. So far, little attention has been paid to the single electrode heat evolution. In galvanic cells working on solid- or liquid-state reactants and products, the

Key words: heat evolution, molten carbonate fuel cells, Peltier entropy, thermal corrosion.

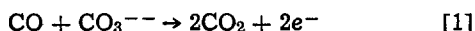
main heat evolution is caused by the polarization losses, whereas in most fuel cells involving a net consumption of gaseous components, the single electrode reactions contribute considerably to the heat evolution at moderate loads. They may give rise to rather large temperature gradients inside the cell. In porous gas diffusion electrodes, temperature gradients may cause convection in the electrolyte film through gradients in

surface tension (1), thus reducing the effective diffusion layer thickness. Furthermore, in high temperature cells where the equilibrium concentration of electrode metal in the electrolyte is not extremely low, temperature gradients along the electrode surface may cause thermal corrosion, ruining the electrode structure by removing active parts of the electrode. This phenomenon has been observed in practice (2) when a leakage of anode gas into the cathode compartment caused a local temperature rise, which removed the electrode area surrounding the leak. Finally, the so-called self-regulation mechanism of porous high temperature cathodes preventing sintering of the porous structure (3) may possibly be explained in terms of a dissolution redeposition reaction caused by temperature gradients in the electrode.

The aim of this paper is a thermodynamic treatment of the single electrode heat evolution in a galvanic cell under load. These heats are calculated for high temperature carbonate fuel cells on the basis of the Peltier entropies determined in part I of this paper (8). An experimental verification of the heat effect is also presented. Finally, some of the effects caused by temperature gradients are briefly discussed.

Single Electrode Heat Balance

Considering the molten carbonate fuel cell anode reaction



the mass fluxes will be as outlined in Fig. 1.

It is noted that a bulk flow of electrolyte is introduced in Fig. 1 in order to obtain the apparent transport numbers of zero for Me^+ and unity for CO_3^{--} with the electrode as reference frame. The transport numbers t_+ and t_- describe the movement of ions relative to the liquid structure and might be determined by the diaphragm method (4). In contrast to the transport numbers with reference to the electrode, these transport numbers do not depend on the nature of the electrode, i.e., whether anion or cation electrodes are used. This distinction between transport numbers relative to the electrodes and to the liquid structure is, in principle, important, since the movement of ions through the liquid structure involves an excess entropy of transport (5). In practice, it is of minor importance for gas electrode reactions, where the main heat effect is caused by the transition from gaseous to condensed state.

In order to determine the heat flow into the electrode compartment during steady-state conditions, we apply the Brønsted heat principle (6)

$$T\delta S'' = -\sum \Delta P_i \delta K_i \quad [2]$$

The heat principle states that in an infinitesimal process transferring the quantity δK_i from the potential P_i to $P_i + \Delta P_i$ the loss of work $-\Delta P_i \delta K_i$ is equivalent to the irreversible heat production $T\delta S''$. In the case of reversibility, the thermodynamic equilibrium conditions may be derived from [2] on the basis of the conditions $\delta S'' = 0$ (7).

Performing an entropy balance on the electrode compartment in the steady state yields

$$\delta S = \delta S' + \delta S'' = 0 \quad [3]$$

where $\delta S'$ is the entropy flow from the surroundings,

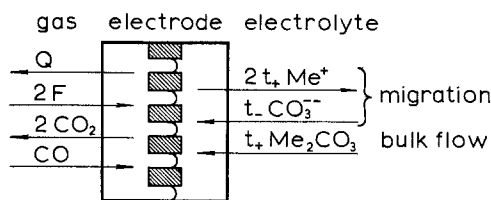


Fig. 1. Mass and heat fluxes into the anode compartment. Electrode reaction: $\text{CO} + \text{CO}_3^{--} \rightarrow 2\text{CO}_2 + 2e^-$.

in the form of heat and reactants. If the heat principle [2] is applied to the process in Fig. 1, we obtain for the transfer of an electric charge δq

$$T\delta S'' = -[(2\mu(\text{CO}_2) + 2\mu(e^-) - \mu(\text{CO}) - \mu(\text{CO}_3^{--}))] \frac{\delta q}{2F} \quad [4]$$

which may be rewritten as

$$T\delta S'' = \left[\left(-\frac{\mu(e^-)}{F} - \phi \right) - \{2\mu(\text{CO}_2) - \mu(\text{CO}) - \mu(\text{CO}_3^{--})\} \frac{1}{2F} \right] \delta q \quad [5]$$

where the term $(-\mu(e^-)/F - \phi)$ is the single electrode potential. In Eq. [5] the chemical potentials refer to the system boundary and since this is chosen to enclose all irreversible processes like diffusion and reaction at the electrode, except for the electric conduction in electrode leads and electrolyte, they do not depend on the degree of irreversibility. As $\delta S'' = 0$ holds for equilibrium conditions, we obtain the relation for the entropy production

$$T\delta S'' = \left[\left(-\frac{\mu(e^-)}{F} - \phi \right) - \left(-\frac{\mu(e^-)}{F} - \phi \right) \right]_{\text{eq}} \delta q = \eta \delta q \quad [6]$$

where η is the overvoltage.

Taking into consideration that species transported by a migration mechanism carry an entropy, S^* , differing from the partial molar entropy (5), the entropy flux into the electrode compartment is, according to Fig. 1, written as

$$\begin{aligned} \delta S' = & -\frac{\delta Q}{T} + [-2S^*(e^-) - 2S(\text{CO}_2) + S(\text{CO}) \\ & - 2t(\text{Me}^+)S^*(\text{Me}^+) + t(\text{CO}_3^{--})S^*(\text{CO}_3^{--}) \\ & + t(\text{Me}^+)S(\text{Me}_2\text{CO}_3)] \frac{\delta q}{2F} \end{aligned} \quad [7]$$

Introducing the excess entropy of transported species,

$\hat{S} = S^* - S$, we obtain

$$\begin{aligned} \delta S' = & -\frac{\delta Q}{T} + [-2S(e^-) - 2S(\text{CO}_2) \\ & + S(\text{CO}) + S(\text{CO}_3^{--}) + \Delta \hat{S}] \frac{\delta q}{2F} \end{aligned}$$

where

$$\begin{aligned} \Delta \hat{S} = & t(\text{CO}_3^{--})\hat{S}(\text{CO}_3^{--}) \\ & - 2t(\text{Me}^+)\hat{S}(\text{Me}^+) - 2\hat{S}(e^-) \end{aligned} \quad [8]$$

Comparing the entropy terms in Eq. [8] with Eq. [4]–[7] in part I of this paper (8), they are identified as the Peltier entropy ΔS_P of the CO electrode reaction. Thus, combining Eq. [3], [6], and [8], we obtain the final expression for the heat evolution due to the partly irreversible n electron single electrode reaction¹

$$\frac{dQ}{dt} = \left(T \frac{\Delta S_P}{nF} + \eta \right) i \quad [9]$$

where the sign convention of a positive anodic current is adopted. Since the term ηi is always positive, whereas

¹ Although Eq. [9], to simplify the notation, has been derived on the basis of the CO_2/CO electrode reaction, the result holds for the "general" reaction $\text{Red} + \text{CO}_3^{--} \rightarrow \text{Ox} + \text{CO}_2 + 2e^-$ where (Ox, Red) is $(\frac{1}{2}\text{O}_2, \text{O}^{2-})$, (CO_2, CO) , $(\text{H}_2\text{O}, \text{H}_2)$, or $(2\text{H}_2\text{O} + \text{CO}_2, \text{CH}_4)$. This is easily seen by substituting $2\mu_{\text{CO}}$, $2S_{\text{CO}}$, μ_{CO_2} , and S_{CO_2} with μ_{Red} , S_{Red} , μ_{Ox} and S_{Ox} and S_{Ox} and S_{CO_2} in the derivation.

the sign of $i\Delta S_P$ changes with the current direction, Eq. [9] holds for both anodic and cathodic reactions.

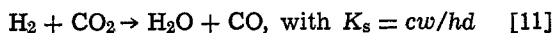
Peltier Entropy of a Mixed Electrode Reaction

As practical fuel cell applications will often involve mixed electrode reactions, like the oxidation of reformed hydrocarbons, we shall go into detail somewhat on the calculation of the Peltier entropy for the C-H-O fuel electrode.

For gaseous mixture of H_2 (h), CO (c), CH_4 (m), H_2O (w), and CO_2 (d) in thermal equilibrium, the Peltier entropy per mole CO_3^{--} has been derived previously (Ref. (8), Eq. [14]). Denoting the partial pressures of the different species by the above-mentioned symbols h , c , etc., we have

$$\Delta S_P(\text{fuel}) = \Delta S_P^0(CO, CO_2) - R \ln \frac{c}{d^2} - RT \frac{\partial}{\partial T} \left(\ln \frac{c}{d^2} \right) \quad [10]$$

It is noted that the Peltier entropy of the mixed electrode reaction does not depend on the kinetically controlled relative contributions from the different electrode reactions. This is due to the assumption of a gas in thermal equilibrium, which implies that the gas phase composition at a total pressure P and a given C/H/O ratio is fixed by the equilibrium conditions



$$\frac{1}{4} [4H_2 + CO_2 \rightarrow CH_4 + 2H_2O],$$

$$\text{with } K_m^{1/4} = \frac{m^{1/4}w^{1/2}}{hd^{1/4}} \quad [12]$$

$$h + c + m + w + d = P \quad [13]$$

A method to calculate the various partial pressures at given P and T from tabulated values of K_s and K_m has been given earlier (9).

The value of the last term in [10] can be calculated on the basis of a mass balance applied to Eq. [11] and [12], using the relations involving the reaction enthalpies: $\partial \ln K_s / \partial T = \Delta H_s^0 / RT^2$ and $\partial \ln K_m^{1/4} / \partial T = \Delta H_m^0 / 4RT^2$. The result can be written as

$$-RT \frac{\partial}{\partial T} \left(\ln \frac{c}{d^2} \right) = - \left(\frac{1}{c} + \frac{2}{d} \right) \frac{P}{T} \frac{\alpha_{22}\Delta H_s^0 - \alpha_{12}\Delta H_m^0/4}{\alpha_{11}\alpha_{22} - \alpha_{12}^2} + \left(\frac{1}{2d} - \frac{1}{2P} \right) \frac{P}{T} \frac{\alpha_{12}\Delta H_s^0 - \alpha_{11}\Delta H_m^0/4}{\alpha_{11}\alpha_{22} - \alpha_{12}^2} \quad [14]$$

where

$$\alpha_{11} = P(1/h + 1/c + 1/w + 1/d) \quad [15]$$

$$\alpha_{12} = P(1/h + 1/2w + 1/4d) \quad [16]$$

$$\alpha_{22} = P(1/h + 1/16m + 1/4w + 1/16d - 1/4P) \quad [17]$$

For fuels containing negligible amounts of CH_4 (high temperatures, low hydrogen contents), $\alpha_{22} \rightarrow \infty$, and [14] reduces to

$$-RT \frac{\partial}{\partial T} \left(\ln \frac{c}{d^2} \right) = - \frac{\Delta H_s^0}{T} \left(\frac{1}{c} + \frac{2}{d} \right) \left(\frac{1}{h} + \frac{1}{d} + \frac{1}{w} + \frac{1}{d} \right) \quad [14a]$$

From the basic data given in Tables I and II, typical heat evolutions at the electrodes of a working molten carbonate cell have been calculated in Table III. It is observed that the heat evolution due to the Peltier effect exceeds the irreversible losses by more than an

Table I. Equilibrium composition of fuel gas at 1 atm and 1000°K. Nominal composition 0.5 atm H_2 + 0.5 atm CO_2 .

	H_2 (h)	CO (c)	CH_4 (m)	H_2O (w)	CO_2 (d)
Partial pressure (atm)	0.269	0.229	7.5×10^{-4}	0.230	0.271

The calculation is based on the thermodynamic data (9): $K_s = 0.723$; $\Delta H_s^0 = 34.8$ kJ/mole; Eq. [11] and $K_m = 0.404$ atm $^{-1/2}$; $\Delta H_m^0/4 = -47.7$ kJ/mole; Eq. [12].

Table II. Peltier entropies at 1 atm and 1000°K

$\Delta S_P(O_2, CO_2)$	= -236 J/mole °K	Calculated from Eq. [2] in Ref. (8)
$\Delta S_P^0(CO, CO_2)$	= -129.5 J/mole °K	Calculated from Eq. [8] in Ref. (8)
$\Delta S_P(\text{fuel})$	= -167 J/mole °K	Calculated from Eq. [10]-[14]

The calculated values are based on $\Delta S_P^0(O_2, CO_2) = -217$ J/mole °K (8).

Cathode gas = 0.14 atm O_2 + 0.28 atm CO + 0.58 atm N_2 .

Anode gas = composition given in Table I.

Table III. Heat evolution in a working molten carbonate fuel cell at 100 mA/cm 2

	Anode	Cathode	Electrolyte
$i T \Delta S_P / 2F$	mW/cm 2		
$i \eta$	mW/cm 2		
dQ/dt	mW/cm 2		
	-86.5	122.3	
	5.0	5.0	5.0
	-81.5	127.3	5.0

The values calculated are based on the data given in Tables I and II and the assumption of a polarization at cathode, anode, and electrolyte corresponding to 0.5 $\Omega \cdot \text{cm}^2$ each.

order of magnitude and equals the amount of heat produced by an overvoltage in the order of 1V. Furthermore, it is noted that about two-thirds of the heat evolved at the cathode is reabsorbed at the anode. Thus, the internal heat fluxes in the working cell are by far larger than would be estimated from a heat balance on the entire cell and rather large temperature gradients will be present in the electrolyte.

Verification of the Heat Effect

The heat effect predicted by Eq. [9] has been experimentally determined in the high temperature cell shown in Fig. 2. Details in the construction of the cell

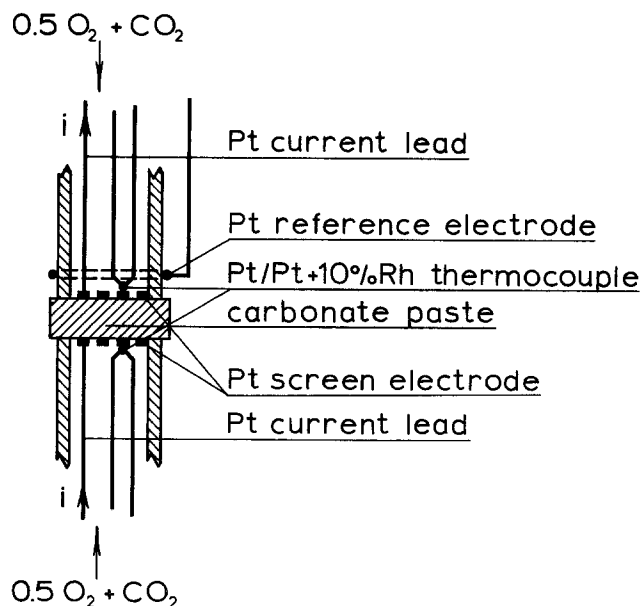
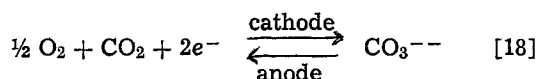


Fig. 2. Cell used for the investigation of heat effect

and the preparation of the carbonate paste electrolyte are given elsewhere (10). The Pt screen electrodes were contacted by Pt/Pt + 10% Rh thermocouples and the temperature rise, ΔT , at each electrode was determined as a function of the current. For practical reasons a mixture of 0.5 vol O_2 + 1 vol CO_2 was applied to both electrodes giving the electrode reactions



For not-too-large current densities, the steady-state overvoltage may be expressed in terms of an electrode resistance, and the temperature rise, being proportional to the heat evolution, can, according to Eq. [9], be written as

$$\Delta T = k \frac{dQ}{dt} = k \left[T \frac{\Delta S_P}{nF} + i(Z_o + R) \right] i \quad [19]$$

where k ($cm^2 \cdot K/W$) is a constant inversely proportional to the local heat conduction, Z_o is the d-c impedance due to the electrode reaction (diffusion, charge transfer etc.), and R is the electrolyte resistance. For symmetry reasons the joule heating will be distributed almost equally between the electrodes and R is thus expected to be approximately half the total anode-cathode electrolyte resistance.

Figures 3 and 4 show the experimental results plotted as $\Delta T/i$ vs. i and, as predicted by Eq. [19], a linear relationship is obtained. It is noted that whereas the cathode reaction causes a temperature rise, the entropy absorption in the anodic direction cools the electrode. From the standard Peltier entropy, ΔS_P^0 , given in part I of this paper, we obtain

$$\Delta S_P(O_2, CO_2) = \Delta S_P^0(O_2, CO_2) + R \ln p_{O_2}^{1/2} p_{CO_2} = -225 \text{ J/mole}^\circ K$$

The polarization resistances were determined from steady-state current-voltage curves measured against the reference electrode and corrected for IR drops. The total electrolyte resistance was measured by a.c. at 10 kHz. The results were

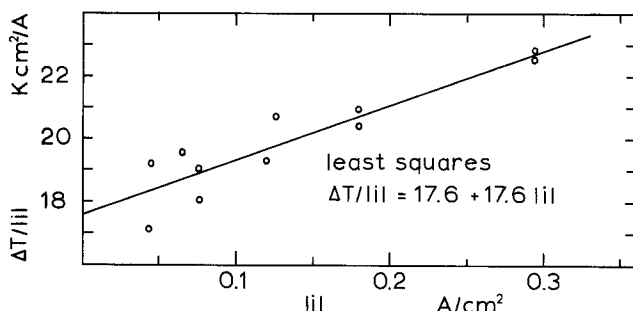


Fig. 3. $\Delta T/i$ vs. i for the cathodic reaction $\frac{1}{2} O_2 + CO_2 + 2e^- \rightarrow CO_3^{--}$.

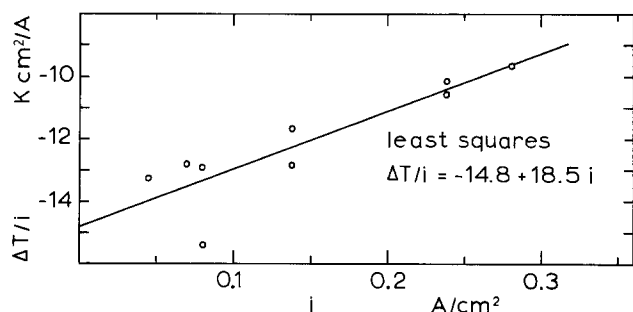


Fig. 4. $\Delta T/i$ vs. i for the anodic reaction $CO_3^{--} \rightarrow \frac{1}{2} O_2 + CO_2 + 2e^-$.

$$\text{cathode} \quad Z_o = 0.50 \Omega \cdot cm^2$$

$$\text{anode} \quad Z_o = 0.55 \Omega \cdot cm^2$$

$$\text{electrolyte} \quad 2R = 1.60 \Omega \cdot cm^2$$

Inserting these values and $T = 1006^\circ K$ in Eq. [19], we obtain the theoretical temperature rise

$$\text{cathode} \quad \Delta T = ik(-1.17 + 1.30i); i < 0$$

$$\text{anode} \quad \Delta T = ik(-1.17 + 1.35i); i > 0$$

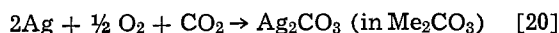
Comparing these expressions with the experimental equations in Fig. 3 and 4, good agreement is obtained with the values $k = 15^\circ K \text{ cm}^2/W$ and $13^\circ K \text{ cm}^2/W$ for cathode and anode, respectively. The somewhat differing k values obtained are probably due to the vertical position of the cell, involving some asymmetry in heat conduction.

It should be noted that the large temperature effect of $35^\circ K \text{ cm}^2/A$ observed here holds for a small cell with 0.8 cm^2 electrode area and 0.4 cm electrolyte thickness. As this cell has severe heat losses through the electrode leads and thermocouples, a larger effect should be expected for practical cells.

Thermal Corrosion

In gas diffusion electrodes, the electrode structure is obviously one of the most important properties. It is known that high temperature fuel cell electrodes, after a certain period of time, obtain a porosity which is essentially determined by the operating conditions and does not depend on the initial electrode structure (3, 10). This very feature of high temperature systems reflects the fact that in the time scale relevant for practical applications, months or even years, the solubility and thus the mobility of electrode material is not negligible. The structural regenerating process, counteracting electrode sintering, has been illustrated by an Ag wire immersion experiment in liquid carbonate (3). It was observed that Ag was removed from the wire below the electrolyte level and redeposited in a porous form at the meniscus. As is shown below, this process, can be explained in terms of thermal corrosion, rather than by gradients in oxygen partial pressure as originally suggested.

The equilibrium



has been studied as a function of temperature for a series of carbonate melts (3). In most cases, the solubility of Ag was found to decrease with increasing temperature. Thus, a thermal process where Ag is dissolved at low temperature and redeposited at higher temperature might be expected to proceed spontaneously. This will indeed be the case as long as there is no electronic contact between the metal at the two temperatures. However, in the immersed wire experiment the contact is established and the redistribution process may be the electrochemical reaction



The temperature dependence of [21] can be determined from the Peltier entropy which may be estimated as

$$\Delta S_P(Ag^+) = S_{Ag} - S_{Ag^+} - S_{e^-} \approx \frac{1}{2} (\Delta S_{Ag_2CO_3} - \Delta S_P(O_2, CO_2)) \quad [22]$$

where $\Delta S_P(O_2, CO_2)$ is the Peltier entropy of the oxygen electrode given by Eq. [3] in part I of this paper (8). $\Delta S_{Ag_2CO_3}$ (cf. [20]) is estimated from the temperature dependence of the solubility equilibrium and we obtain a value in the order of $100 \text{ J/mole}^\circ K$ for the Peltier entropy of reaction [21] in equilibrium with $p_{O_2} = p_{CO_2} = 1 \text{ atm}$. As this entropy difference is positive, in contrast to the entropy difference for the chemical dissolution of Ag [20], a transport of Ag from

high to low temperature through the electrochemical mechanism involves a simultaneous transfer of entropy from high to low temperature and the process is spontaneous. Thus, the effect of the electronic contact is a reversing of the thermal corrosion process. Aten *et al.* (11) observed and interpreted similar phenomena for silver and copper in 1925 and in aqueous solutions also this kind of process has been observed for Ag electrodes and explained in terms of a thermal emf (12), which is equivalent to the entropy argument

In the immersion wire experiment as well as in single laboratory fuel cells, the electrode leads will act as heat sinks and create a temperature gradient at the electrolyte surface. Thus, the thermal process will remove electrode material dipping into the electrolyte and deposit material at the gas side of the electrode. This continuous renewal of the electrode surface may be, at least partially, responsible for the stability of high temperature porous electrodes (3, 10). In a fuel cell battery the effect of the thermal redistribution is difficult to predict since the temperature gradients depend on the position inside the battery. However, the existence of this process means that temperature gradients should be taken into account in the construction of high temperature systems in order to ensure long-term stability. Temperature gradients along the electrodes should be reduced as far as possible. Since Peltier entropies are dependent on the various partial pressures, large fuel and oxygen conversions per single pass may entail these gradients and thus active parts of the electrodes may be removed completely and redeposited elsewhere. An extreme case has been observed by Trachtenberg (2). Furthermore, cathodes should be kept under constant load in order to reduce the equilibrium concentration of ions from the electrodes in the electrolyte.

Finally, it should be mentioned that temperature gradients may contribute to the formation of the electrolyte films in porous gas electrodes through the Marangoni effect, i.e., flow due to gradients in surface tension. Lightfoot (1) has treated this effect quantitatively and concludes that temperature gradients as low as a few tenths of a degree per centimeter may produce a 1 μm film, which is the order of magnitude observed in practice (13, 14).

Acknowledgments

The authors are indebted to Mr. H. J. J. van Ballegoy who carried out the experimental verification of the heat effect. The many valuable discussions with B. K. Andersen and other colleagues are greatly appreciated. This work has been supported by Statens Teknisk Videnskabelige Fond.

Manuscript submitted May 27, 1976; revised manuscript received Oct. 8, 1976. This was Paper 171 pre-

sented at the New York, New York, Meeting of the Society, May 4-9, 1969.

Any discussion of this paper will appear in a Discussion Section to be published in the December 1977 JOURNAL. All discussions for the December 1977 Discussion Section should be submitted by Aug. 1, 1977.

LIST OF SYMBOLS

F	Faraday constant (C/mole)
H	enthalpy (J/mole)
i	current (A)
K	equilibrium constant
n	number of electrons
P	pressure
p	partial pressure (atm)
q	electric charge (C)
Q	heat (J)
S	entropy (J/mole °K)
ΔS_p	Peltier entropy (J/mole °K)
S'	entropy flow (J/mole °K)
S''	irreversible entropy production (J/mole °K)
S*	entropy of transported species (J/mole °K)
\hat{S}	excess entropy of transported species (J/mole °K)
t	time (sec)
t_i	transport number
T	temperature (°K)
η	overvoltage (V)
ϕ	electric potential (V)
μ	chemical potential (J/mole)
μ	electrochemical potential (J/mole)

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